

# Tuning the hydrogen evolution reaction at the Pt(111) surface with graphene and non-precious metal

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## Abstract

The hydrogen evolution reaction (HER) is the process where protons from the electrolyte combine with the electrons from the metal electrode catalyst to produce atomic hydrogen adsorbed on the metal surface. The reaction ends when the adsorbed hydrogen atoms then form molecular hydrogen and thereby desorb from the surface of the catalyst. Therefore, the bonding between the catalyst and the proton should be optimal such as to favour the adsorption of the H atoms but at the same time not too strong to hinder the H<sub>2</sub> molecular formation. The main application of HER is in an electrolyser occurring at the cathodic half-cell where the efficiency of the cathode material determines the efficiency of the whole device. In the current study we present a combined experimental and theoretical study of the state of the art metallic electrocatalyst platinum (Pt) by tuning its reactivity towards HER with graphene (Gr) and iron (Fe). Experimental methods such as electrochemical scanning tunnelling microscopy (EC-STM), and cyclic voltammetry are combinedly used to image and measure the reactivity simultaneously during the reaction. Structure and further chemical properties are explored by employing low-energy electron diffraction (LEED) and X-ray photoemission spectroscopy (XPS). Using density functional theory (DFT) the HER reactivity in the two systems namely Gr/Pt(111) and Gr/Fe/Pt(111) is investigated computationally. In the former the presence of Gr is observed to increase the selectivity/permeability towards protons [1] and at the same time weaken the binding of H compared to that on bare Pt [2]. This favours the diffusion of the H atoms at the interface and hence H<sub>2</sub> molecular formation. The H adsorption weakens further in the presence of intercalated Fe at the Gr/Pt(111) interface, pointing towards the possibility of replacing the expensive Pt by combining Gr and Fe.

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## References

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